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Synthesis and Electrochemical Properties of Homo- and Heterodimetallic Diethynylethene Bisphthalocyaninato Complexes

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A series of molecular dyads, consisting of two homo- or heterodimetallic ($M = M' = Zn^{II}$ or $M = Zn^{II}$, $M' = Co^{II}$) phthalocyaninato complexes bridged by mono- and bis-DEE [(*E*)-1,2-diethynylethene, (*E*)-hex-3-ene-1,5-diyne] fragments, was prepared by Pd(0)-catalyzed cross-coupling reactions or by oxidative Glaser−Hay coupling, respectively. The electronic properties of these extensively linearly π-conjugated materials were investigated by UV−visible spectroscopy and electrochemically [cyclic voltammetry and Osteryoung square wave voltammetry], and the spectroscopic data were compared to those of previously prepared phthalocyanine (Pc) dyads, in which benzene rings of the two Pc chromophores are bridged by ethynediyl and buta-1,3-diynediyl linkers, respectively. Whereas the electronic absorption spectra did not reveal significant bathochromic shifts of the Soret and Q-bands with increasing extension of the linearly π-conjugated nanomaterials, substantial electronic communication between the two Pc units in the dyads across the DEE bridges was revealed in the electrochemical studies.

Introduction

Phthalocyanines (Pcs)[1] and related compounds, such as subphthalocyanines[2] and hemiporphyrazines,[3] are excellent building blocks for the construction of multipurpose materials with unusual physical properties[4] such as nonlinear optical qualities.[5]

In an attempt to establish the potential electronic- and photonic-base cooperation between individual subunits of phthalocyanine in Pc-dyads, we have recently reported compounds in which two phthalocyanine rings are bound together through ethynyl linkages.[6] These kinds of spacers are able to mediate unusually high excitonic and electronic coupling between chromophore centers.[7] Few examples describing electronic interactions in planar Pc-dimers have been reported.[8] In the present paper, we describe the preparation of a series of highly conjugated phthalocyanine-[(*E*)-1,2-diethynylethene] (DEE)[9] systems and confirmation for the first time of the existence of substantial electronic communication between the two phthalocyanine units in alkynyl linked Pc-dyads.[10]

In this regard, homo- and heterodimetallic and push−pull unsymmetrically substituted DEE-bisphthalocyanine compounds were prepared using Pd(0)-mediated cross-coupling methodologies. These compounds were studied electrochemically, and the results compared to those of other Pc-dimers previously described by us.[6]

Results and Discussion

The synthesis of homodimetallic (*E*)-1,2-diethynylethene (DEE) bis(tri-*tert*-butyl)phthalocyaninates **3a,b** was car-

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(10) Electronic coupling between two porphyrin moieties through DEE linkers has been recently described by some of our group. See ref 7c.

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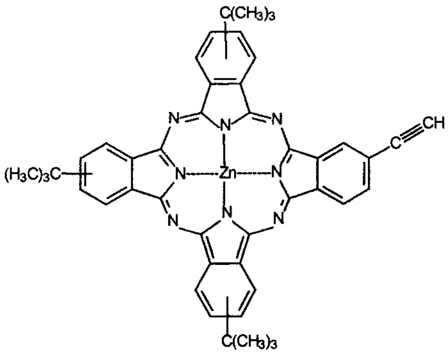

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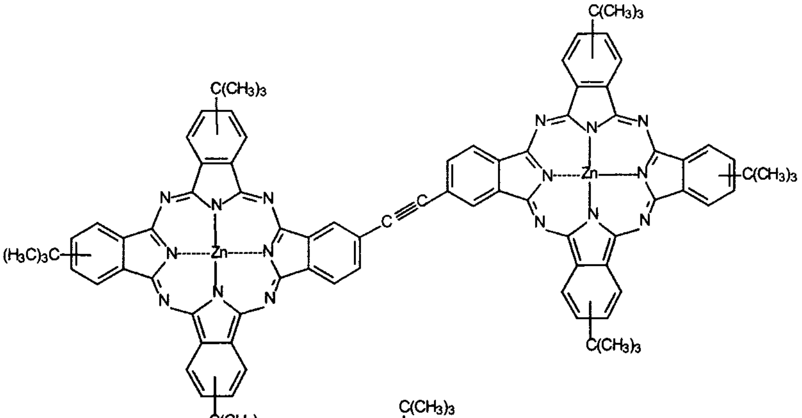

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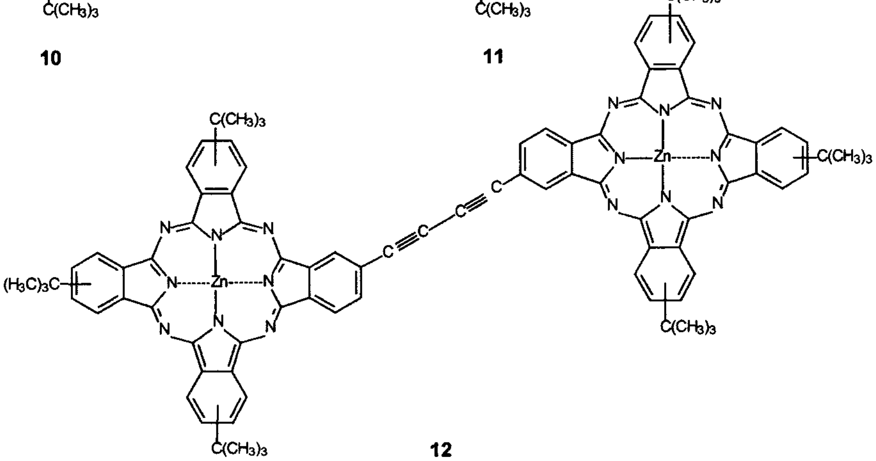

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ried out by metal-mediated cross-coupling[11] of (*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}hex-3-ene-1,5-diyne (**2**)[9a] with the corresponding iodophthalocyanines **1a,b** (Scheme 1). The reaction was performed in the presence of a catalyst formed in situ by adding triphenylarsine to tris(dibenzylidenacetone)dipalladium(0) [$Pd_2(dba)_3$], conditions which prevent the homocoupling reaction of the dialkynyl compound.[11a] The change in color of the reaction mixture from blue to green when the Pc-dimers begin to form is quite remarkable.

The tri-*tert*-butyliodophthalocyaninato cobalt(II) (**1a**) was prepared following a procedure similar to that described by us for the preparation of **1b**.[6b] Thus, the statistical condensation of 4-iodophthalonitrile[13] with 3 equiv of 4-*tert*-butylphthalonitrile[14] in the presence of cobalt(II) chloride (1 equiv) yielded a mixture of the tetra-*tert*-butylphthalocyaninato cobalt(II) and the unsymmetrical iodo-Pc **1a**, which were separated by column chromatography.

For the preparation of heterodimetallic DEE-bis(tri-*tert*-butyl)phthalocyaninato **3c** (Scheme 1), an unsymmetrically substituted DEE unit **4**[15] was employed. Thus, treatment of DEE compound **2** with BuLi (1 equiv) in dry THF at −78 °C and further addition of Me_3SiCl yielded the unsymmetrical DEE compound **4**.[15] This compound was then reacted with the iodo-Pcs **1a,b** (Scheme 1) under the same conditions mentioned above for the preparation of **3a,b** to yield the corresponding conjugated unsymmetrical Pcs **5a,b** in 36% and 70% yield, respectively. The protecting TMS group on the ethynyl functionality of these Pcs was then removed to yield the unsymmetrical ethynyl Pcs **6a,b** in excellent yield (86−91%). The ethynylphthalocyaninato cobalt(II) **6a** and the iodophthalocyaninato zinc(II) **1b** were then reacted under cross-coupling conditions similar to those described above to yield the heterodimetallic DEE dimer **3c** (Scheme 1) in good yield.

The UV−visible spectrum of homodimetallic dimer **3b** is shown in Figure 1 and compared to those of its precursor **1b** and other ethynyl conjugated species, such as **6b** and the buta-1,3-diynediyl bridged bis(tri-*tert*-butyl)phthalocyaninato zinc(II)-zinc(II) **12** previously prepared by us.

The UV−visible spectra (Figure 1) show a splitting and a slighly bathochromic shift of the Q-band for **6b** and **12** and to a lesser extent for **3b** compared to **1b**, a result of the increasing conjugation. However, the optical features of the new system **3b** differ slightly from those of the unsymmetric terminal alkyne **6b** and of the buta-1,3-diynediyl-bridged dimer **12**. Compound **3b** shows a weakly split Q-band at 678 nm with a shoulder at 710 nm, in contrast to the clear splitting observed for **6b** and **12**. Moreover the new species **3b** does not show clear red shifting of the Q-band despite the more extended conjugation of the dyad compared to **6b** and **12**. The close resemblance between the UV−visible spectra of **6b** and **12**, and even of **3b**, suggests that saturation of the optical properties in the series occurs already at the stage of the buta-1,3-diynediyl-bridged compound **12**.[7c] In this way,

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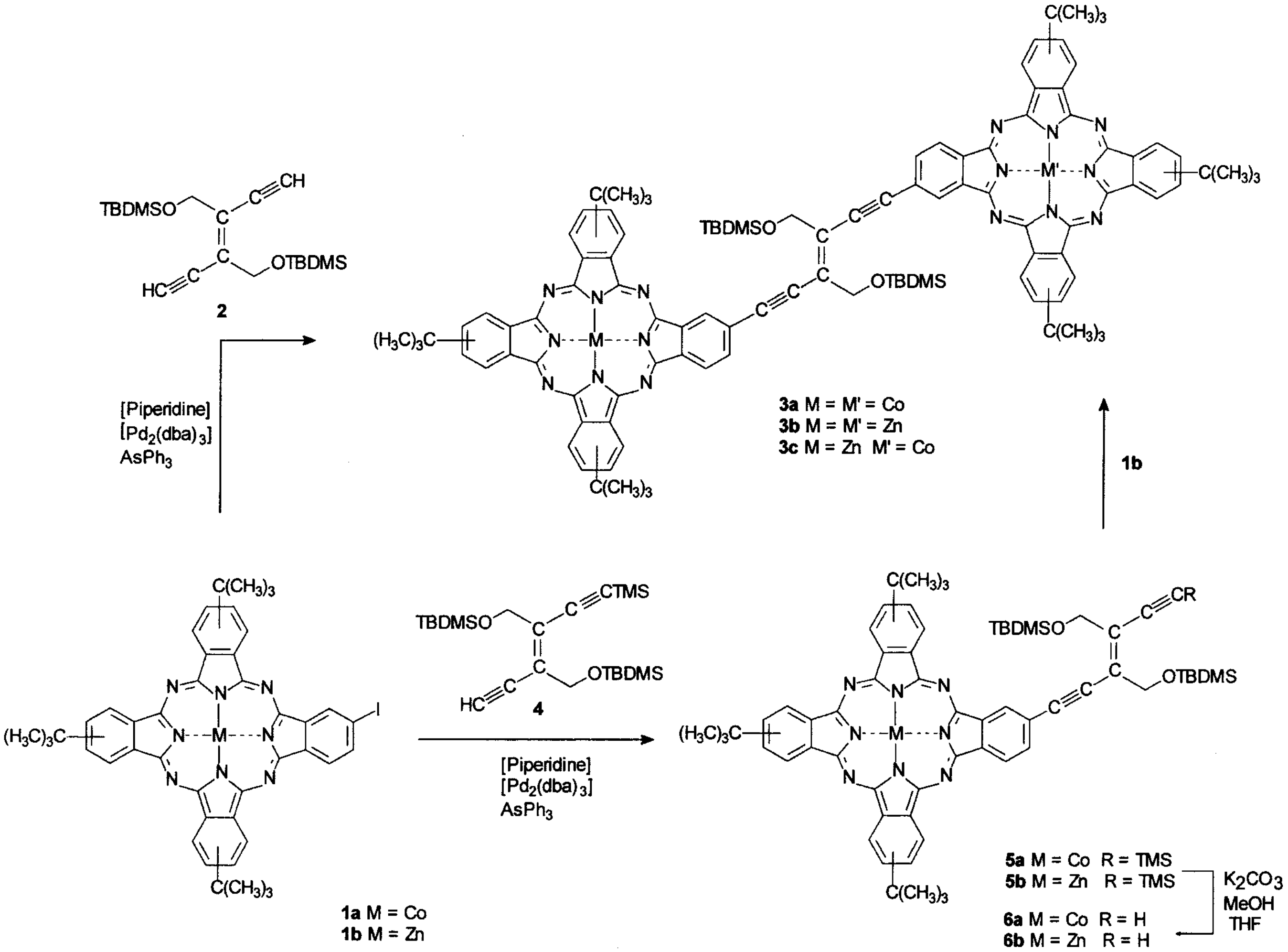
Scheme 1. Synthesis of DEE-Bridged Bisphthalocyaninato Complexes 3a−c



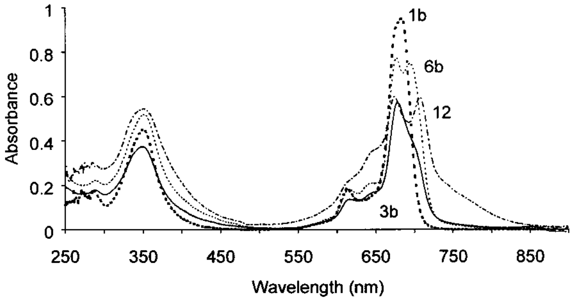


Figure 1. Electronic spectra in $CHCl_3$ of **3b** (1.2×10^{-5} M) (continuous line), **6b** (4.1×10^{-6} M) (dotted line), **1b** (6.2×10^{-6} M) (dashed line), and **12** (1.1×10^{-5} M) (dotted-dashed line).

the formal substitution of the buta-1,3-diynediyl linker in **12** by a DEE unit in **3b** does not modify the electronic distribution of the phthalocyanine units appreciably. A similar result is observed when comparing the electronic spectra of **3b** with those of the model bisphthalocyanine **11**[6b] having only one carbon−carbon triple bond as spacer, or the spectra of dimer **3c** with that for its precursor, DEE-Pc **6a**.

The electrochemistry of ethynyl-phthalocyanine **10**, Pc-dyads **11** and **12**, and the series of conjugated phthalocyanine-DEE compounds **3a−c** was studied using cyclic (CV) and Osteryoung Square Wave Voltammetric (OSWV) methods. The results of the CV experiments are summarized in Table 1 (reduction) and Table 2 (oxidation).

Table 1. $E_{1/2}$ **Values for the Reduction Processes as the Average of the Cathodic and Anodic Peak Potentials**[a]

compd	E_1 (V)	E_2 (V)	E_3 (V)	E_4 (V)	E_5 (V)
10	−1.42(80)	−1.77(60)	−2.37[b](243)		
11	−1.42(106)	−1.80(106)	−2.43[b](136)		
12	−1.39(106)	−1.71(46)	−2.43[b](222)		
3a	[c]	−1.71(78)	−1.96(88)	−2.47(110)	
3b	−1.47(117)	−1.82(170)			
3c	−0.82(115)	−1.47(75)	−1.72(59)	−1.87(48)	−2.45(122)
9	−1.35(75)	−1.58[b](96)			
8a	−1.52(87)	−1.97[b](29)	−2.39(71)		
8b	−1.52(61)	−1.70(48)	−1.87(44)	−2.08(57)	
6a	−0.81(117)	−1.69(76)	−1.91(98)		

[a] All values are based on the Fc/Fc$^+$ redox couple as internal reference. ΔE_p is mV. [b] Irreversible processes. [c] Difficult to measure as a result of a peak broadness.

The ethynylated monomeric Pc **10** showed two reversible one-electron reduction processes based on the phthalocyanine (Figure 2), each with a ΔE_{pp} ($= E_p^{red} - E_p^{ox}$) of 60−80 mV. The ethynediyl-linked Pc-dyad **11** and the single homodimetallic DEE-bridged Pc dimer **3b** showed two chemically reversible two-electron reduction processes (Figure 2), but with ΔE_{pp} values of 106−117 mV for the first reduction, indicative of electronic coupling between the Pc units (see below). Controlled potential electrolysis was performed in dry DMF under vacuum for compound **3b**. Electrolysis showed that the first reduction of this compound is a two-electron process (−1.9 e/molecule). In general, reductions became easier upon increasing the length of the acetylenic bridge. The first

Table 2. $E_{1/2}$ Values of Oxidation Processes as the Average of the Cathodic and Anodic Peak Potentials[a]

compd	E_1 (V)	E_2 (V)
10	0.12[b](53)	*c*
11	0.26	0.59
12	0.13	0.57
3a	0.22	0.56
3b	0.25	0.58
3c	0.27	0.60
9	0.06	*c*
8a	*c*	0.61
8b	0.24	*c*
6a	0.22	0.57

[a] All values are based on the Fc/Fc$^+$ redox couple as internal reference. [b] Reversible processes. [c] Difficult to measure due to a peak broadness.

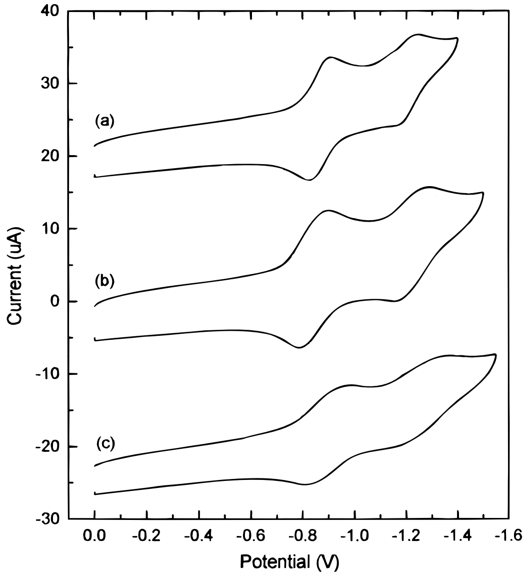


Figure 2. Cyclic voltammograms of (a) **10**, (b) **11**, and (c) **3b**. CV experiments were performed in DMF at room temperature with a scan rate 100 mV/s. A Ag/AgCl electrode was used as a reference electrode, and ferrocene was added as an internal reference. TBAPF$_6$ (tetrabutylammonium hexafluorophosphate) was added as supporting electrolyte.

reduction at −1.42 V (vs Fc/Fc$^+$) for **11** was anodically shifted to −1.39 V for **12**. Figure 3a shows the OSWV of the reduction processes for compound **3a**. The first reduction process of the DEE-bridged Pc dimer **3a** is a Co(II)−Co(I) process.[1a] The second reduction at −1.71 V for **3a** corresponds to the simultaneous reduction of the DEE substituent and the phthalocyanine moiety based on the value observed for monomeric Pc **6a**.[9b] The reduction processes of the heterodimetallic DEE-bridged Pc dimer **3c** correspond almost exactly to those of the individual redox steps of the constituent monomers (Zn−Pc and Co−Pc).

The homodimetallic Pc dimers **11**, **12**, and **3b** show clear evidence of electronic coupling between the Pcs from the CV results. The value of the peak to peak separation (ΔE_{pp}) for the first reduction of these compounds is large, 106 mV for **11** and **12** and 117 mV for **3b**. Although electrochemically irreversible behavior (slow electron transfer kinetics) could be the cause of this kind of peak broadness, comparison with the results for monomeric Pc indicates that this is probably not the case. The first reduction wave for the monomer Pc **10** is a quasireversible one-electron process with $\Delta E_{pp} = 80$ mV.

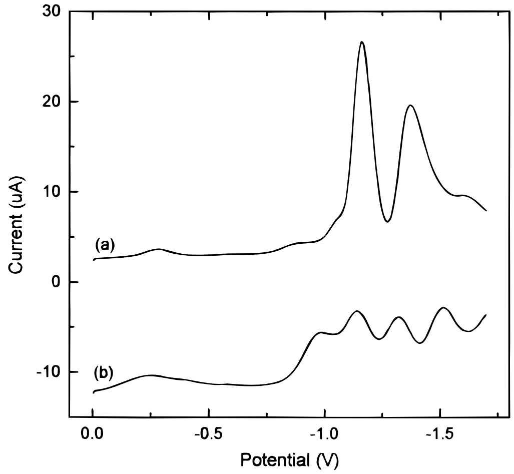


Figure 3. Osteryoung square wave voltammograms (reduction) of compounds (a) **3a**, and (b) **8b**. OSWV experiments were performed in DMF at room temperature with a scan rate of 100 mV/s. A Ag/AgCl electrode was used as a reference electrode, and ferrocene was added as an internal reference. TBAPF$_6$ (tetrabutylammonium hexafluorophosphate) was added as supporting electrolyte.

Table 3. Calculated $\Delta E_{1/2}$ Values of the First and Second Reduction Processes from CV[a]

compd	$\Delta E_{1/2}$ (mV)	HOMO−LUMO gap (mV)
10[b]	−341	1540
11	−75	1065
12	−75	920
3b	−83	1102
9	−52	842

[a] All values are based on the Ag/AgCl reference. [b] From the experimental CV.

Similar behavior would be expected for the dimers in the absence of electron coupling. In addition, as already mentioned, controlled potential electrolysis of Pc dimer **3b** confirmed the two-electron nature of the first reduction wave.

Taube et al. introduced a method to determine the half-wave potentials ($\Delta E_{1/2}$) for closely spaced two-electron charge transfers by cyclic voltammetry, such as those observed for **11, 12**, and **3b**.[16] The half-wave potentials of the Pc-dyads determined using this method are summarized in Table 3. The calculated differences in the first two-electron reduction potentials ($\Delta E_{1/2}$) for the Pc-dyads are a measure of the degree of electronic coupling between the two phthalocyanine units bridged by DEE or alkynyl moieties.[7c,17] The extensively conjugated single DEE-bridged Pc-dyad **3b** shows the strongest electronic coupling between the two PC units, as expected.

Electronic coupling between two porphyrin moieties through DEE linkers has also been recently reported by some of our group.[7c] When compared to an analogous compound, a single DEE-bridged porphyrin-dyad, phthalocyanine-dyads exhibit weaker electronic coupling.[7c] This is evident from the CV results. Whereas Pc-dyad **3b** has a separation gap of 117 mV for the first two-electron reductions, an analogous porphyrin-dyad has a value of 140 mV. This result was anticipated because the pyrrolic systems in porphyrin and phthalocyanine dyads behave

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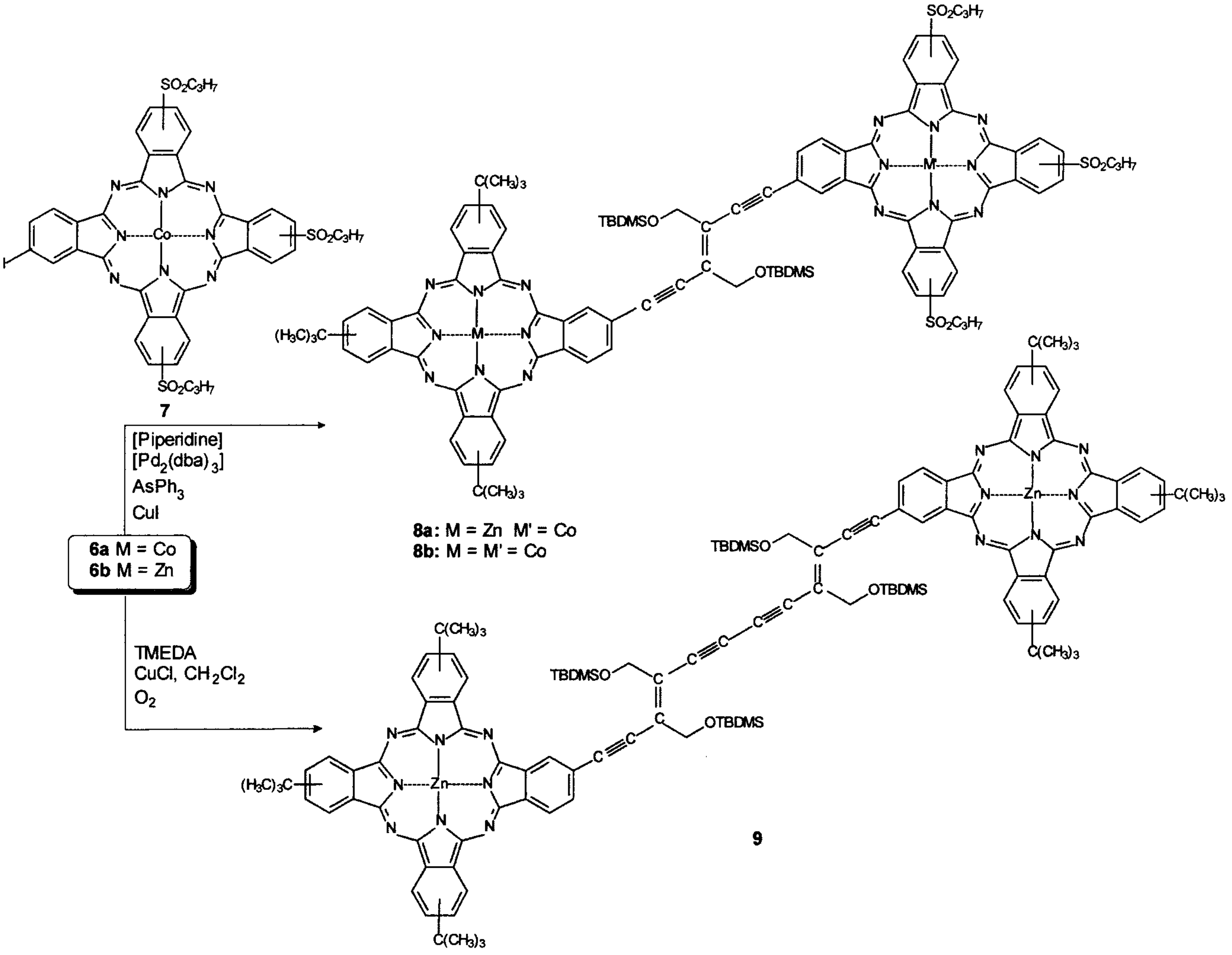
Scheme 2. Synthesis of DEE-Bridged Bisphthalocyaninato Complexes 8a,b and 9



substantially differently. In Pc-dyads, electrons are more confined to the macrocyclic rings than those in the analogous porphyrin system; presumably the extra benzene rings fused to the pyrrol rings in Pcs reduce the overall electron delocalization.

Most oxidation processes of phthalocyanine dyads show chemically irreversible behavior. There is also a tendency toward easier oxidation upon increasing the degree of substitution, from $+0.26$ V (vs Fc/Fc^+) for **11** to $+0.13$ V for **12**. The first oxidation [Co(II)-Co(III)] of DEE-bridged Pc dimer **3a** shows a weak irreversible peak at $+0.22$ V (vs Fc/Fc^+). The oxidations of Pc-dyads **3b** and **11** from OSWV show two separated one-electron processes.

The HOMO−LUMO gap, calculated as the difference of the first oxidation and the first reduction potentials, is also shown in Table 3. Because of the irreversible nature of the oxidation process, we used the anodic peak potential as the first oxidation value and the calculated $\Delta E_{1/2}{}^1$ for the first reduction potential. Because of the anodic shift for reduction and the cathodic shift for oxidation, the HOMO−LUMO gap decreases upon increasing the linear π-conjugation length (see series **10**−**12**).

We were especially interested in the preparation of highly conjugated push−pull homo- and heterodimetallic bisphthalocyanines for nonlinear optical applications.[6b] Thus, we prepared dimers **8a,b** having electron-donating and electron-withdrawing substituents in each of the two Pc subunits by reaction of unsymmetrical ethynyl derivatives **6a,b** and tris(propylsulfonyl)iodo-Pc **7**[6b] (Scheme 2). The cross-coupling reaction was performed using a catalyst formed by $[Pd_2(dba)_3]$ and $AsPh_3$[11a] in the presence of a small amount of CuI. When the reaction was carried out in the absence of CuI, no cross-coupling compounds were detected. To avoid the homo-coupling side reaction of the ethynyl derivatives **6a,b** promoted by copper(I), these compounds were added to the reaction mixture after treatment of the iodo-Pc **7** with the catalyst. The reaction was monitored by TLC until all starting Pcs were converted into the new blue-green species. No homo-coupling compounds were detected under these conditions.

The UV−visible spectra of these new push−pull systems **8a,b** are presented in Figure 4. The Q-bands of these new species are not split and are centered around 670 nm, slightly shifted to the blue compared with those of their precursors **6a,b**. Compound **8a** shows a broad absorption at 630 nm, thus indicating aggregation[18] of the metallomacrocycles. Aggregation effects in these kinds of systems is a new observation, although it was proposed previously by us.[6b]

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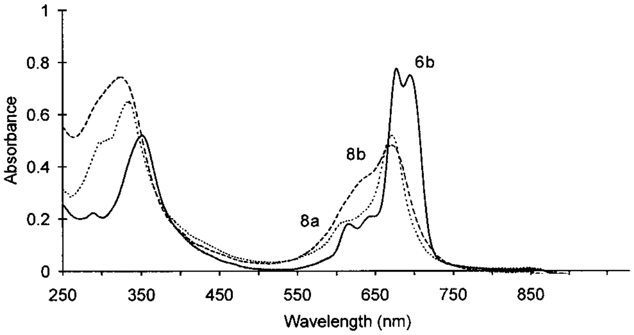

Figure 4. Electronic spectra in $CHCl_3$ of **6b** (4.1×10^{-6} M) (continuous line), **8a** (1.05×10^{-5} M) (dotted line), and **8b** (1.2×10^{-5} M) (dashed line).

The electrochemistry of push−pull unsymmetrically substituted DEE-bisphthalocyanine compounds **8a,b** was also studied by CV and OSWV. The first reduction, which is difficult to measure by CV, for compounds **8a,b** corresponds to the [Co(II)-Co(I)] process. The homodimetallic unsymmetrically substituted DEE-bisphthalocyanine **8b** shows the expected split pattern by OSWV (Figure 3b). The second and third reductions of **8b** were each split into two reduction processes when compared to those of the homodimetallic symmetrically substituted DEE-bisphthalocyanine **3a** (Figure 3a).

To prepare an even more exclusively linearly conjugated Pc dimer, such as **9**, we also performed the homocoupling reaction of ethynyl derivative **6b** (Scheme 2). This connection was carried out in dry dichloromethane containing molecular sieves, *N*,*N*,*N*′,*N*′-tetramethylethynylenediamine (TMEDA), and CuCl in the presence of O_2.[19]

The UV−visible spectrum of this compound is almost identical to that of its precursor **6b**, thus confirming that saturation of the optical properties had already occurred at the linear conjugation length of **6b**.

The electrochemical behavior of the bis-DEE-bridged Pc dimer **9** shows a tendency similar to that measured for the buta-1,3-diynediyl linked Pc-dyad **12**. The reductions became significantly easier upon increasing the length of the DEE bridge. Thus, the first reduction at −1.47 V (vs Fc/Fc$^+$) for the mono-DEE-bridged Pc dyad **3b** was anodically shifted to −1.35 V for the bis-DEE-bridged Pc dyad **9**. The oxidation process also became easier upon increasing the length of the DEE bridge, from +0.25 V for **3b** to +0.06 V for **9**.

Conclusions

Two novel types of extensively linearly π-conjugated molecular dyads, in which two Pc chromophores are linked by mono- or bis-DEE bridges, were prepared. UV−visible investigations did not reveal a significant reduction of the optical gap with increasing extension of the linearly π-conjugated chromophore. On the other hand, electrochemical studies clearly showed an enhanced ease of both the first reduction and oxidation steps when the bridge between the two Pc moieties was increased from a mono-DEE to a bis-DEE fragment. Similar results were obtained when the bridge between the two Pc moieties in the dyad was extended from a simple ethynediyl to a buta-1,3-diynediyl fragment. The CV data provided for the first time evidence for electronic communication between two phthalocyanine moieties in alkynyl-linked Pc-dyads. A comparison between linearly π-conjugated Pc-dyads and porphyrin-dyads with DEE linkers revealed that electron delocalization is more effective in the latter; we take this as evidence for the insulating properties of the extra benzene rings (with the localized aromatic π-electron sextets) in the Pc chromophore. Investigations into the nonlinear optical properties of the novel, highly polarizable Pc materials, described in this manuscript, are now under way.

Experimental Section

General Procedures. Melting points are uncorrected. NMR spectra were recorded at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR. The mass spectra were determined on a VG AutoSpec. All tetrasubstituted phthalocyanines synthesized were obtained as a mixture of 2,9,16,23-, 2,10,16,24-, 2,9,-17,24-, and 2,9,16,24-regioisomers. For this reason, compounds **3a**−**c**, **8a**,**b**, and **9** are also mixtures of the corresponding regioisomers. The ^{13}C NMR spectra of these compounds are characterized by very low intensity peaks corresponding to aromatic carbons difficult to identify and a large number of signals in the aliphatic region, mainly because compounds **1a**, **3a**−**c**, **8a**,**b**, and **9** are actually mixtures of several regioisomers, as mentioned above. Being uninformative, these spectra have not been included in the Experimental Section.

Tri-*tert*-butyl-iodophthalocyaninato cobalt(II) (1a). A mixture of 4-*tert*-butylphthalonitrile[14] (500 mg, 2.71 mmol) and 4-iodophthalonitrile[13] (114 mg, 0.45 mmol) was heated at reflux in dimethylaminoethanol (DMAE) (2 mL) under argon for 12 h in the presence of $CoCl_2$ (60 mg, 0.45 mmol). After concentration under reduced pressure, the blue solid obtained was extracted with CH_2Cl_2 and washed with water. Compound **1a** was separated from the tetra-*tert*-butylphthalocyaninato cobalt(II) by chromatography on silica gel using a mixture of hexane and dioxane (4:1) as eluent. The product was then washed with hot MeOH, filtered, and dried to yield 94 mg (15%) of **1a**. Mp > 300 °C. ^1H NMR ($CDCl_3$) δ: 8.8−8.1 (m, 12H), 1.6 (broad signal, 27H). FT-IR (KBr) ν: 3444, 2955, 1330, 1092 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ε): 670 (5.2), 606 (4.6), 329 nm (4.9). MS−FAB [*m*-NBA (*m*-nitrobenzyl alcohol)] *m*/*z* (%): 866 (100) [(M + H)$^+$], 850 (26) [(M − CH_3)$^+$]. Anal. Calcd for $C_{44}H_{39}N_8ICo$: C, 61.05; H, 4.54; N, 12.94. Found: C, 61.38; H, 5.05; N, 12.88.

(*E*)-Bis[(tri-*tert*-butylphthalocyaninato)cobalt(II)-cobalt(II) or zinc(II)-zinc(II)]-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]-methyl}-hex-3-ene-1,5-diyne (3a,b). General Procedure. A mixture of **1a**,**b** (36 mg, 0.041 mmol), [Pd_2(dba)$_3$]·$CHCl_3$ (20 mg, 0.021 mmol), $AsPh_3$ (42 mg, 0.14 mmol), and (*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]methyl}hex-3-ene-1,5-diyne[12] (15 mg, 0.042 mmol) (**2**) was stirred at 35 °C in freshly distilled and deaerated piperidine under argon until the starting phthalocyanines had reacted. The solution was then concentrated under reduced pressure, and the green oil obtained was extracted with CH_2Cl_2 and washed with water. Compound **3a** was purified by chromatography on silica gel using a mixture of hexane/dioxane (10:1) as eluent, whereas for **3b** a mixture of CH_2Cl_2/2-propanol (100:1) was used.

3a. Reaction time: 12 h. Yield: 20 mg (24%). Mp > 300 °C. ^1H NMR ($CDCl_3$) δ: 8.0−7.0 (6 × m, 24H), 4.61 (m, 4H), 1.6 (broad signal, 54H), 1.10 (broad signal, 18H), 0.10 (m, 12H). FT-IR (KBr) ν: 3466, 2911, 2355, 1650, 1616, 1255, 1088, 800, 761 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ε): 694 (sh) (4.2), 670 (4.3), 611 nm (sh) (3.8). MS−FAB (*m*-NBA) *m*/*z* (%): 1839 (100) [(M + H)$^+$], 1724 (68) [(M − 2 × C(CH_3)$_3$)$^+$], 1707 (20) [(M − OTMDMS)$^+$]. Anal. Calcd for $C_{108}H_{112}N_{16}O_2Si_2Co_2 \cdot 6H_2O$: C, 66.26; H, 6.34; N, 11.45. Found: C, 66.62; H, 6.02; N, 11.74.

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3b. Reaction time: 4 h. Yield: 21 mg (34%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.8−7.0 (6 × m, 24H), 4.58 (m, 4H), 1.58 (broad signal, 54H), 1.10 (broad signal, 18H), 0.10 (m, 12H). FT-IR (KBr) ν: 3444, 2944, 2355, 1255, 1083 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 680 (4.7), 618 (4.1), 348 nm (4.6). MS−FAB (*m*-NBA) *m*/*z* (%): 1853−1849 (isotopic pattern) (100) [(M + H)$^+$]. Anal. Calcd for $C_{108}H_{112}N_{16}O_2Si_2Zn_25H_2O$: C, 66.71; H, 6.33; N, 11.53. Found: C, 66.36; H, 5.94; N, 11.73.

(*E*)-Bis[(tri-*tert*-butylphthalocyaninato)zinc(II)-cobalt(II)]3,4-bis{[(*tert*-butyl)dimethylsilyloxy]-methyl}hex-3-ene-1,5-diyne (3c). To 24 mg (0.027 mmol) of **1b** in freshly distilled and deaerated piperidine in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ (18 mg, 0.002 mmol) and $AsPh_3$ (12 mg, 0.038 mmol) was added a solution of **6a**[15] (66 mg, 0.056 mmol) in piperidine, and the mixture was stirred for 4 h at 35 °C. The solvent was then removed under reduced pressure, and the green oil obtained was dissolved in CH_2Cl_2 and washed with water. The crude reaction was purified by column chromatograpy on silica gel using toluene as eluent to yield 32 mg (67%) of **3c** as a green solid. Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.9−7.0 (6 × m, 24H), 4.60 (m, 4H), 1.58 (broad signal, 54H), 1.10 (broad signal, 18H), 0.09 (m, 12H). FT-IR (KBr) ν: 3455, 2955, 2355, 1644, 1616, 1255, 1088, 800 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 679 (4.5), 614 (3.8), 314 nm (4.3). MS−FAB (*m*-NBA) *m*/*z* (%): 1848−1846 (isotopic pattern) (47) [(M + H)$^+$]. Anal. Calcd for $C_{108}H_{112}N_{16}O_2Si_2CoZnH_2O$: C, 67.02; H, 6.35; N, 11.58. Found: C, 67.15; H, 5.98; N, 11.89.

(*E*)-Tri-*tert*-butyl-[(3,4-bis{[(*tert*-butyl)dimethylsilyloxy]-methyl}-6-(trimethylsilyl)]hex-3-ene-1,5-diynyl-phthalocyaninato metal(II) (5a,b). General Procedure. A mixture of **1a**,**b** (88 mg, 0.100 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (24 mg, 0.026 mmol), $AsPh_3$ (48 mg, 0.156 mmol,) and (*E*)-3,4-bis{[(*tert*-butyl)dimethylsilyloxy]-methyl}-1-(trimethylsilyl)hex-3-ene-1,5-diyne (**4**)[12] (0.042 mg, 0.078 mmol) was stirred at 35 °C in freshly distilled and deaerated piperidine under argon for 2 h. The solution was then concentrated under reduced pressure, and the oil obtained was extracted with CH_2Cl_2 and washed with water. Compound **5a** was purified by chromatography on silica gel using toluene as eluent, whereas for **5b** a mixture of CH_2Cl_2/MeOH (100:1) was employed.

5a. Blue solid. Yield: 42 mg (36%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.7−6.9 (4 × m, 12H), 4.50 (m, 4H), 1.54 (broad signal, 27H), 1.10 (broad signal, 18H), 0.2−0.1 (m, 21H). FT-IR (KBr) ν: 3425, 2947, 2859, 2370, 1651, 1585, 1250, 1088, 762, 695 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 683(4.9), 671(4.9), 610 (4.4), 328 nm (5.3). MS−FAB (*m*-NBA) *m*/*z* (%): 1174 (100) [(M + H)$^+$], 1158 (19) [(M − CH_3)$^+$]. Anal. Calcd for $C_{67}H_{82}N_8O_2Si_3Co2H_2O$: C, 66.47; H, 7.16; N, 9.26. Found: C, 66.19; H, 7.53; N, 9.24.

5b. Green solid. Yield 84 mg (70%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.7−6.9 (4 × m, 12H), 4.50 (m, 4H), 1.54 (s, 27H), 1.10 (broad signal, 18H), 0.2−0.1 (m, 21H). FT-IR (KBr) ν: 3433, 2955, 2855, 2344, 1611, 1250, 1088, 808 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 693(5.1), 679 (5.1), 616 (4.4), 352 nm (4.9). MS−FAB (*m*-NBA) *m*/*z* (%): 1181−1179 (isotopic pattern) (100) [(M + H)$^+$], 1165−1163 (isotopic pattern) (21) [(M-CH_3)$^+$]. Anal. Calcd for $C_{67}H_{82}N_8O_2Si_3Zn3H_2O$: C, 65.15; H, 7.18; N, 9.07. Found: C, 65.18; H, 7.52; N, 8.71.

(*E*)-Tri-*tert*-butyl-[(3,4-bis{[(*tert*-butyl)dimethylsilyloxy]-methyl}-6-ethynyl)]-hex-3-ene-1,5-diynyl-phthalocyaninato Metal(II) (6a,b). General Procedure. A mixture of **5a** or **5b** (52 mg, 0.045 mmol) and K_2CO_3 (6 mg, 0.043 mmol) was dissolved in MeOH and wet THF (4:1) and stirred for 2 h at room temperature. Then, the solvent was removed under reduced pressure, and the crude reaction was diluted with CH_2Cl_2 and washed with water. The compounds should be stored at low temperature (−20 °C) to avoid decomposition.

6a. Blue solid; 42 mg (86%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.8−7.0 (4 × m, 12H), 3.62 (s, 1H), 1.54 (s, 27H), 1.10 (broad signal, 18H), 0.09 (m, 12H). FT-IR (KBr) ν: 3420, 2945, 2360, 1650, 1581, 1250, 1089, 765 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 686(5.0), 612 (4.4), 330 nm (5.0). MS−FAB (*m*-NBA) *m*/*z* (%): 1102 (100) [(M + H)$^+$], 1086 (15) [(M − CH_3)$^+$]. Anal. Calcd for $C_{64}H_{74}N_8O_2Si_2Co3H_2O$: C, 70.04; H, 7.35; N, 10.21. Found: C, 69.97; H, 7.25; N, 10.42.

6b. Green solid; 69 mg (91%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.7−7.0 (broad signal, 12H), 4.50 (m, 4H), 3.56 (broad signal, 1H), 1.54 (s, 27H), 1.10 (broad signal, 18H), 0.08 (m, 12H). FT-IR (KBr) ν: 2955, 2911, 2344, 1250, 1088, 1016, 800 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 694 (5.1), 678 (5.1), 616 (4.4), 351 nm (4.9). MS−FAB (*m*-NBA) *m*/*z* (%): 1109−1107 (isotopic pattern) (100) [(M + H)$^+$], 1093−1091 (isotopic pattern) (17) [(M − CH_3)$^+$]. Anal. Calcd for $C_{64}H_{74}N_8O_2Si_2ZnH_2O$: C, 70.04; H, 6.98; N, 10.21. Found: C,70.41; H, 7.23; N, 10.54.

(*E*)-[Tri-*tert*-butylphthalocyaninato Metal(II)-tri-(propylsulfonyl)phthalocyaninato Cobalt(II)]3,4-bis{[(*tert*-butyl)dimethylsilyloxy]-methyl}-hex-3-ene-1,5-diyne (8a,b). General Procedure. A 30 mg (0.027 mmol) portion of **7**[6b] was stirred in freshly distilled and deaerated piperidine in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ (15 mg, 0.016 mmol), $AsPh_3$ (30 mg, 0.098 mmol), and CuI (3 mg, 0.015 mmol). A solution of **6a** or **6b** (30 mg, 0.027 mmol) in piperidine was then added, and the mixture was stirred at 35 °C. The reaction was monitored by TLC until all the starting phthalocyanines had reacted. The solvent was then removed under reduced pressure, and the blue-green oil obtained was dissolved in CH_2Cl_2 and washed with water. The bisphthalocyaninates **8a**,**b** were purified by chromatography on silica gel using a mixture of CH_2Cl_2/2-propanol (100:1) as eluent.

8a. Reaction time: 6 h. Yield: 24 mg (45%). Mp > 300 C. ^{1}H NMR ($CDCl_3$) δ: 8.4−6.9 (6 × m, 24H), 3.05 (m, 6H), 1.8 (m, 6H), 1.58 (broad signal, 27H), 1.2−0.9 (broad signal, 27H), 0.1 (m, 12H). FT-IR (KBr) ν: 3427, 2920, 2345, 1620, 1256, 1095, 1032, 798 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 680 (4.6), 616 (sh) (4.2), 329 nm (4.6). MS−FAB (*m*-NBA) *m*/*z* (%): 1990 (100) [(M + H)$^+$]. Anal. Calcd for $C_{105}H_{106}N_{16}O_8S_3Si_2Co_24H_2O$: C, 61.14; H, 5.57; N, 10.87. Found: C, 61.51; H, 5.97; N, 11.10.

8b. Reaction time: 12 h. Yield: 27 mg (47%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 8.4−6.9 (6 × m, 24H), 3.1 (m, 6H), 1.8 (m, 6H), 1.60 (broad signal, 27H), 1.2−0.9 (m, 27H), 0.1 (m, 12H). FT-IR (KBr) ν: 3427, 2920, 2345, 1620, 1256, 1095, 1032, 798 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 676 (4.5), 639 (sh) (4.0), 608 (sh) (4.1), 336 nm (4.6). MS−FAB (*m*-NBA) *m*/*z* (%): 1996−1994 (isotopic pattern) (100) [(M + H)$^+$]. Anal. Calcd for $C_{105}H_{106}N_{16}O_8S_3Si_2CoZn5H_2O$: C, 60.47; H, 5.61; N, 10.75. Found: C, 60.68; H, 6.00; N, 11.13.

(*E,E*)-Bis[(tri-*tert*-butylphthalocyaninato)zinc(II)-zinc(II)]3,4,9,10-tetrakis-{[(*tert*-butyl)dimethylsilyloxy]-methyl}-dodeca-3,9-dien-1,5,7,11-tetrayne (9). A 3.48 mg (0.036 mmol) portion of CuCl was added to a solution of **6b** (26 mg, 0.036 mmol) in a mixture of dry CH_2Cl_2 (5 mL) and TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (0.006 mL) containing 4 Å molecular sieves. After 12 h of stirring under an O_2 atmosphere, water was added, and the reaction mixture was extracted with CH_2Cl_2 until the washings were colorless. Yield: 20 mg (75%). Mp > 300 °C. ^{1}H NMR ($CDCl_3$) δ: 8.0−7.0 (6 × m, 24H), 4.55 (m, 8H), 1.57 (broad signal, 54H), 1.1 (m, 36H), 0.1 (m, 24H). FT-IR (KBr) ν: 3500, 2890, 2335, 1610, 1256, 1091, 1032, 790 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 696 (4.1), 678 (4.1), 644 (sh) (3.6), 616 (sh) (3.5), 350 nm (4.0). MS−FAB (*m*-NBA) *m*/*z* (%): 2216−2212 (isotopic pattern) (18) [(M + H)$^+$], 1851−1854 (isotopic pattern) (100) [(M − 3 × SiOTBDMS)$^+$].

Electrochemistry. The potentiostat used to make all electrochemical measurements was a BAS 100 W electrochemical analyzer. A 3 mm glassy carbon electrode was used as a working electrode, and Ag/AgCl was used as a reference electrode. Ferrocene was added as an internal potential reference ,and all of the values are reported vs the Fc/Fc$^+$ couple. Dry dimethylformamide (DMF) was used as solvent under an argon atmosphere. The compound concentration was typically 0.5 mM; 100 mM $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) was added as supporting electrolyte after being recrystallized twice from ethanol and water (95/5%) and dried in a vacuum. A typical scan rate was

100 mV/s. An electrochemical experiment using a minielectrode in 50 μL of solvent was performed for compound **9**.

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